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CONCENTRATION, TEMPERATURE, AND DENSITY IN A HYDROGEN-AIR FLAME BY EXCIMER-INDUCED RAMAN SCATTERING

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Background The prospect of "low-cost" earth-to-orbit flight has renewed interest in the design and development of supersonic combustors. To study prototype supersonic combustors, laser diagnostics with improved capabilities are needed to meet the stringent requirements of high-speed flows. These improved capabilities include: 1) increased time-and-space resolution as the Kolmogorov microscales in high-speed flows are smaller and 2) increased data accumulation rates to obtain sufficient turbulence statistics in short duration blow-down experiments. In addition, high-speed combustion requires laser techniques that instantaneously and simultaneously sense the local gas thermodynamic and chemical properties. Unlike subsonic combustion flows where often the chemistry is "fast" and equilibrium chemistry assumptions can often be made in high-speed reacting flows the fluid times are short and the chemistry proceeds at a finite rate. Finite-rate chemistry in a supersonic combustor can affect the thrust (from slow radical recombination), shock positions (through changes in the ratio of specific heats, and the combustion efficiency (from flame extinction effects). To assess the finite-rate chemistry effects, the local instantaneous fuel/air mixture ratio (mixture fraction) and the degree of reaction must be determined. This requires laser measurements that simultaneously sense many properties (temperature, concentration of reactants and products).

Single-pulse, vibrational Raman scattering (VRS) is an attractive laser diagnostic for the study of supersonic hydrogen-air combustion. The VRS technique gives a complete thermodynamic description of the gas mixture at a point in the reacting flow. Single-pulse, vibrational Raman scattering can simultaneously provide independent measurements of density, temperature, and concentration of each major species (H_2, H_2O, O_2 and N_2) in a hydrogen/air turbulent combustor.[1] Also the pressure can be calculated using the ideal gas law. However, single-pulse VRS systems in current use for measurement of turbulent combustion have a number of shortcomings when applied to supersonic flows: 1) slow repetition rate (1-5Hz), 2) poor spatial resolution ($0.5 \times 0.3 \times 0.3 mm^3$) and 3) marginal time resolution ($1 \mu s$). Most of these shortcomings are due to the use of visible wavelength flash-lamp pumped dye lasers.

The advent of UV excimer lasers allows the possibility of dramatic improvements in the single-pulse, vibrational Raman scattering. The excimer based VRS probe will greatly improve repetition rate (100-500 Hz), spatial resolution ($0.1 \times 0.1 \times 0.1 mm^3$) and time resolution (30ns). These improvements result from the lower divergence of the UV excimer, higher repetition rate, and the increased Raman cross-sections (15-20 times higher) at ultra-violet (UV) wavelengths. With this increased capability, single-pulse vibrational Raman scattering promises to be an ideal non-intrusive probe for the study of hypersonic propulsion flows.

Theory Spontaneous vibrational Raman scattering is one of the many scattering processes that can be used for local measurement of temperature and species concentration. Although spontaneous Raman scattering is weak compared to other light scattering processes such as Rayleigh scattering, CARS and laser-induced fluorescence, it has the advantages of 1) gas species selectivity, 2) simple interpretation of the signal (no collisional quenching), and 3) simultaneous multi-property determination (major species concentration, temperature, and pressure). In vibrational Raman scattering, the scattered light is either red shifted (Stokes) or blue shifted (anti-Stokes) when the vigrational level, V, of the molecule is either increased, $\Delta V=+1$, or decreased, $\Delta V=-1$. The selection rules for the rotational quantum number, J, are $\Delta J=0$, +2, or -2. The Q branch spectrum ($\Delta J=0$) is much stronger than the O branch ($\Delta J=-2$) or S branch ($\Delta J=+2$). The radiant flux of Stokes Q branch ($V \rightarrow V+1$) is given by [2]:

$$S(V,J) \propto \frac{g(2J+1)\,(V+1)\,\nu^4 C_o}{Q_{rot} Q_{vib}} \exp\left(\frac{hc\,G(V,J)}{kT}\right) \qquad [1]$$

Here S(V<J) is the radiant flux, v is the frequency (Hz) of the Raman light for the specific transition, and g is the nuclear spin factor. The molecular partition functions for rotation and vibration are Q_{rot} and Q_{vib}, respectively. Also h is Planck's constant, k is Boltzmann's constant, T is temperature, c is the speed of light, and G(V,J) is the molecular term value in wavenumbers. The constant C_o is proportional to the vigrational Raman cross-section, $\sigma=C_o\nu^4$. The anti-Stokes ($V+1 \rightarrow V$) radiant flux is identical to Eqn. 1 except from the term (V+1) is replaced by (V). Examples of Q branch Stokes and anti-Stokes scattering calculated from Eqn.1 are shown in Fig. 1. Only even values of J are shown. The spectra are calculated for excimer laser (248.4 nm) induced scattering rom nitrogen at room temperature (300 K) and flame temperature (2400 K). To evaluate the concentration and temperature by VRS, one must consider the number of scattered photons measured by a detection system. The number of detected Stokes photons is given by the following working equation:

$$N_S = Q_S C_S \Omega L n \sigma_S E/(h\nu_S) \qquad [2]$$

where

C_S = optical efficiency at ν_S
E = laser energy (joules)
ν_S = Stokes frequency (Hz)
L = detected length of laser beam (m)
n = number density of molecules (#./m^3)
Q_S = detector quantum efficiency at ν_S
σ_S = Raman cross-section at ν_S (m^2/sr)
Ω = solid angle of the optics (sr)

The frequency of the Stokes light is given by, $\nu_S = \nu_L - \nu_R$, where ν_L is the incident light frequency and ν_R is the Raman shift. The number density of detected anti-Stokes photons is given by a Boltzmann ratio,

$$N_a = KN_S\,(\nu_a/\nu_S)^3 \exp[-T_v/T] \qquad [3]$$

where, $K=(Q_aC_a)/(Q_sC_s)$. The anti Stokes shift is $\nu_a=\nu_L+\nu_R$ and T_v is the characteristic vibrational temperature of the gas species (33357.6 K for nitrogen). The optical efficiency and quantum efficiency at the anti-Stokes wavelength are given by C_a and Q_a, respectively. The number density of any species will be determined from the Stokes scattering (Eqn. 2). The temperature can be determined from the ratic of Stokes to anti-Stokes signals given by Eqn. 3,

$$T = \frac{T_v}{\ln(N_s/N_a) + 3\ln(\nu_a/\nu_s) + \ln(K)} \qquad [4]$$

The pressure can then be determined from the ideal gas law, P=nkT when n is the total number density of all the major species in the gas. Since Raman scattering is weak, the photon noise will be the major contribution to the signal uncertainty. The photon detection follows Poisson statistics such that the uncertainty (or standard deviation) of the Stokes and anti-Stokes measurement is, $S_{Ns}=\sqrt{N_s}$ and $S_{Na}=\sqrt{N_a}$. The uncertainty in the concentration is, $S_n=\sqrt{N_s}$. The uncertainty in the temperature is[3],

$$\frac{S_T}{T} = \frac{1}{T}\left[\left(\frac{\partial T}{\partial N_s} S_{Ns}\right)^2 + \left(\frac{\partial T}{\partial N_a} S_{Ns}\right)^2\right]^{1/2} \qquad [5]$$

where

$$\frac{\partial T}{\partial N_s} = \frac{-(T_v/N_s)}{[\ln(N_s/N_a) + 3\ln(\nu_a/\nu_s) + \ln(K)]^2} \qquad [6]$$

$$\frac{\partial T}{\partial N_a} = \frac{-(T_v/N_a)}{[\ln(N_s/N_a) + 3\ln(\nu_a/\nu_s) + \ln(K)]^2} \qquad [7]$$

In order to determine the accuracy of the VRS technique in high temperature, hypersonic engine inlets; the experimental uncertainties for vibrational Raman scattering in air were calculated for the measurement of the Stokes nitrogen signal, the anti-Stokes nitrogen signal, the anti-Stokes nitrogen signal, temperature, and pressure. These were determined as a function of temperature, pressure, laser wavelength, and laser energy. The optical properties were assumed to be constant for the Stokes and anti-Stokes scattering (K=1). Thus the subscripts (a and s) on the optical constants can be dropped. The assumed optical and molecular parameters were:

C_s	= 0.06	Ω	= 0.35 sr (f/1.5 Optics)	ν_R	= 6.993 x 10^{13} sec^{-1} (2331 cm^{-1})
Q_p	= 0.2	L	= 0.2 mm	T_v	= 3357.6 K (Nitrogen)

Measured cross-sections for vibrational Raman scattering[4] were used. Typical results of these calculations are shown in Fig. 2.

Experimental Results The UV excimer based Raman system is shown in Fig. 3. A KrF excimer laser (broadband, 0.5 nm linewidth) produces 200 mj/pulse of unpolarized light at 248 nm. The excimer laser pulses are focused to 0.2 mm diameter in the H_2/Air flame. The unwanted polarization of the laser is dumped with a Brewster angle window and the laser intensity in the focal volume is about 10 GW/cm^2. The UV Raman light is collected by a f/1.5 quartz lens and focused by a f/10 quartz lens onto the entrance slit of a triple grating spectrometer giving a spatial resolution of about 0.2 mm. The triple spectrometer gives excellent rejection of the 248 nm light (10^{-12}) with multi-wavelength detection. All the Raman lines can be detected simultaneously by multiple photomultipliers recorded by a multi-channel gated integrator. Typical spectra of vibrational Raman scattering in room air in shown Fig. 4a.

Hydrogen/air flame measurements of Raman scattering at 248 nm were made in an adiabatic, multi-element, "Hencken" flat flame burner at stoichiometric conditions. The flame spectrum is shown in Fig. 4b. and the Stokes Raman signal from nitrogen can be seen. However the other regions of the spectrum contain strong fluorescence that is similar to the two-photon photo-fragmentation spectrum of water measured by Fotakis et al[5]. Fotakis irradiated water vapor with a broadband KrF excimer at 0.1 GW/cm^2 and attributed the resulting fluorescence to photo-dissociation of water vapor and the subsequent production of excited that fluoresces in the region near 250 nm. In this stoichiometric hydrogen flame, the fluorescence could also be due to direct excitation of the radicals in the flame. In lean flames, fluorescence of vibrationally excited O_2 can also occur. Andersen et al6 has reported excitation of , O_2, and H_2O with a tunable, narrowband KrF excimer (0.002 nm linewidth). VRS measurements may by possible using a tunable KrF excimer that is tuned to avoid resonant transitions near 248 nm. Since a tunable, narrowband laser is not available for this work, application of the VRS technique in flames is being pursued using the XeF transition (350 nm) in the excimer laser.

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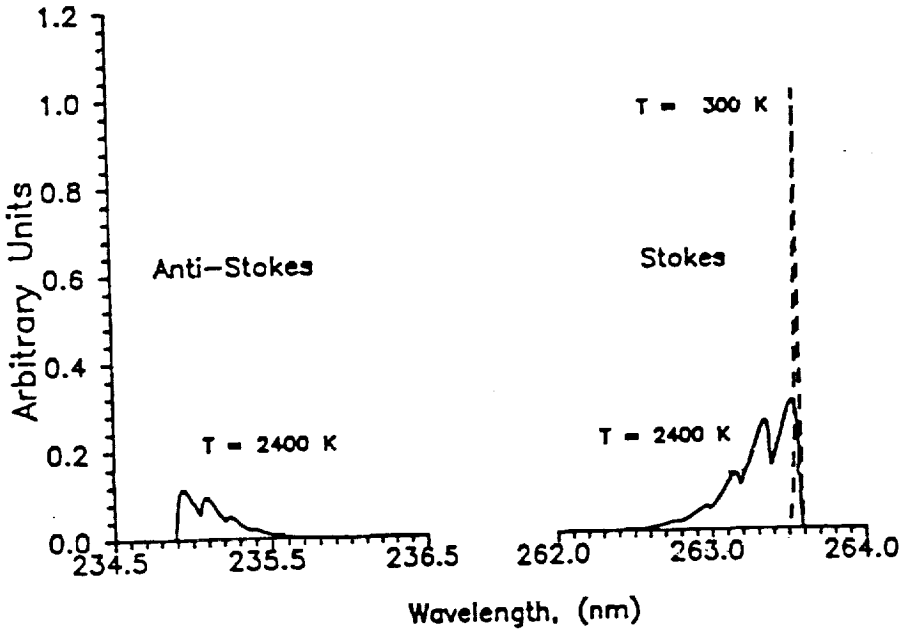

Figure 1. Vibrational Raman Spectra of Nitrogen Induced by a KrF Excimer Laser (248.4 nm)

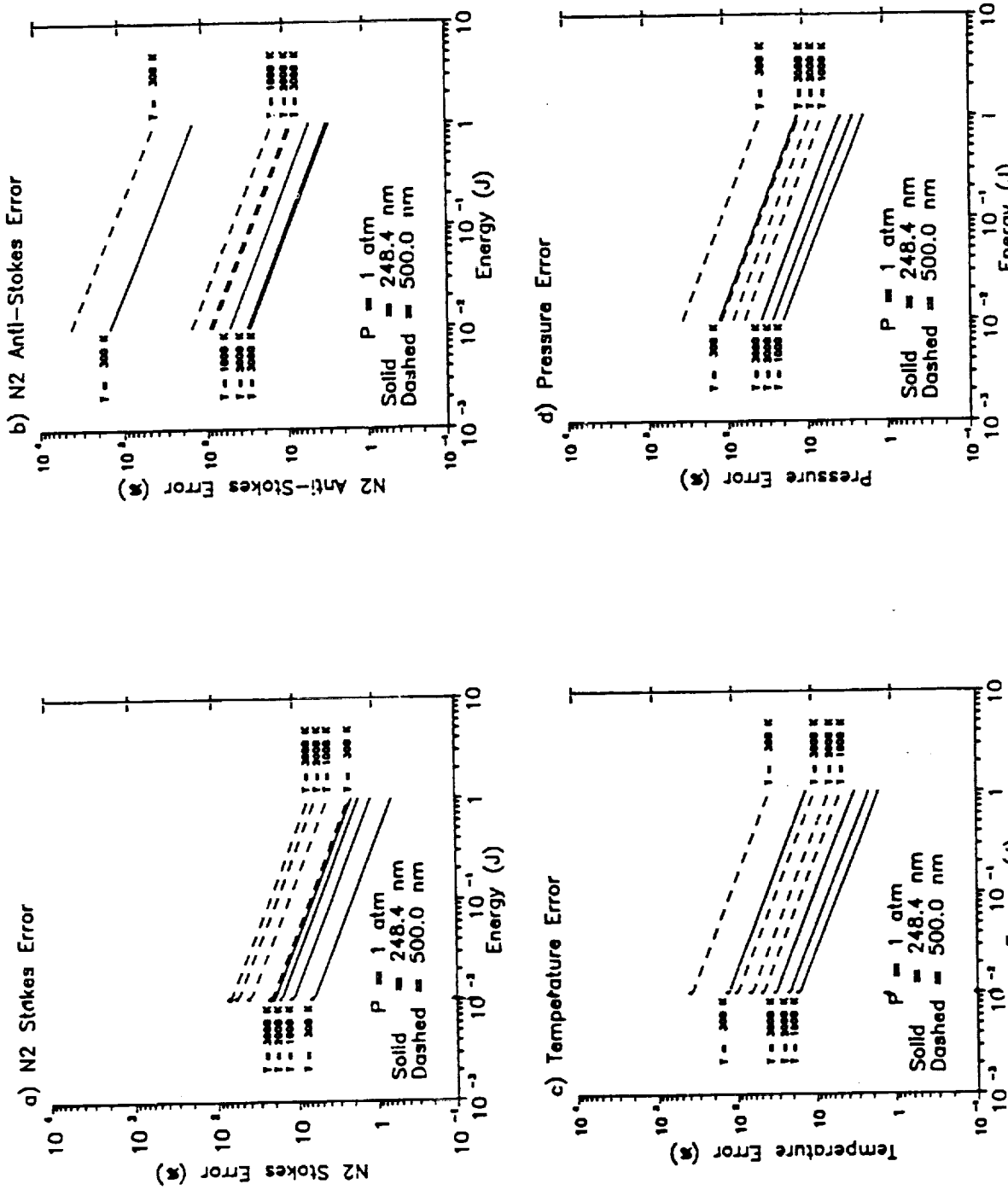

Figure 2. Accuracy of Vibrational Raman Measurements in Air

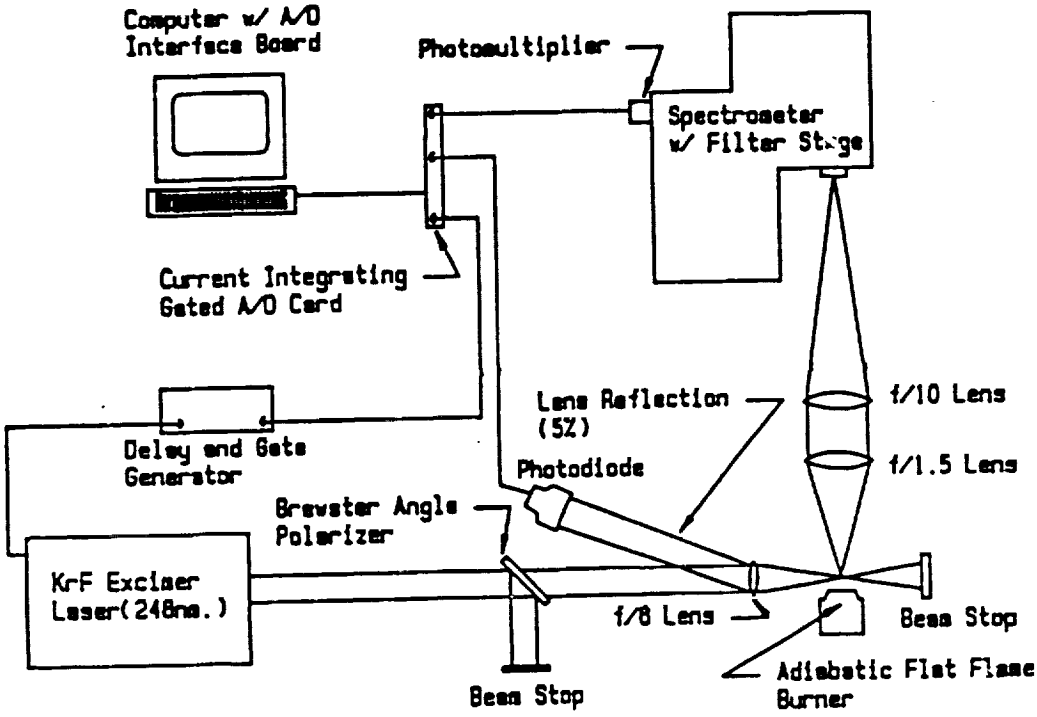

Figure 3. Schematic of Vibrational Raman Scattering System

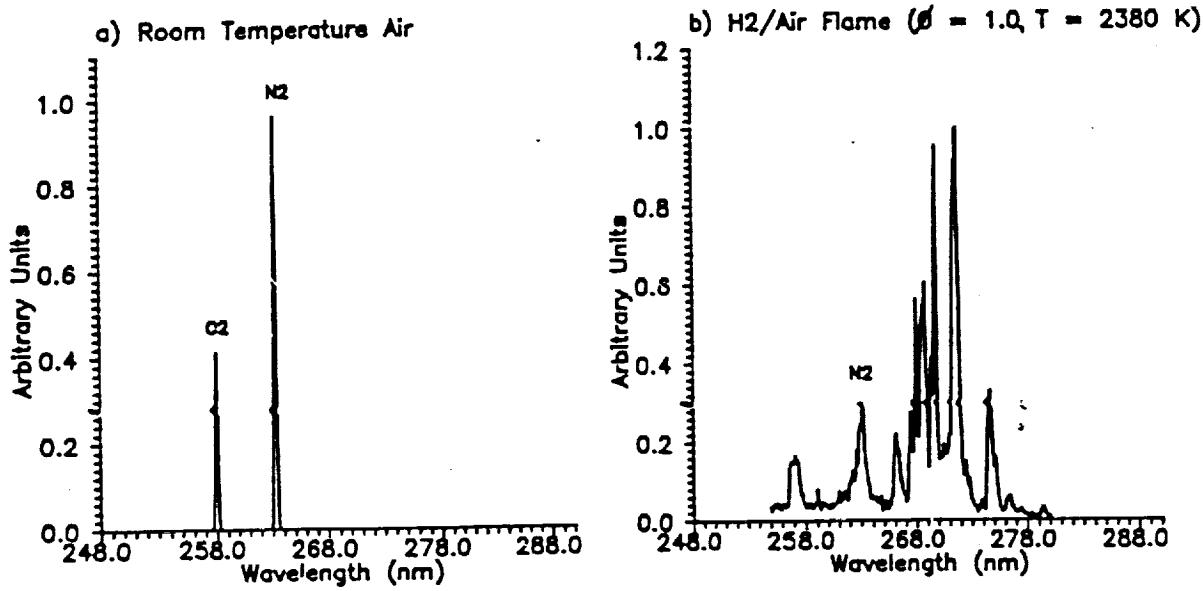

Figure 4. Measured Spectra of Vibration Raman Scattering from a KrF Excimer Laser (248.4 nm)